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Waste Management 62 (2017) 255–261

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

An overview: Recycling of solid barley waste generated as a by-product in distillery and brewery

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ARTICLE INFO

Article history:
Received 16 July 2016
Revised 20 January 2017
Accepted 11 February 2017
Available online 22 February 2017

Keywords:
Biomass
Bioconversion
Bioproducts
Animal feed
Solid waste

ABSTRACT

This overview has focused on the options available for the utilisation of residual-biomass generated in distillery and brewery for the production of added-value products. Bio-processing approaches have been reviewed and discussed for the economical bioconversion and utilisation of this waste for the production of bioproducts, such as lactic acid, enzymes, xylitol and animal feed. Though this overview provides several options for the bioprocessing of this residual material, a more suitable one could be chosen according to the processing-facilities available and the amount of residue available in local area. The feasibility of any chosen process should be evaluated on the basis of cost of material available, its local utilisation for animal feed, and the overall economical advantages that could be gained by changing its current traditional landfill use to produce higher added value products.

Contents

1. Introduction

The distilled-spirits industry has a large market in various countries producing distilled alcohol (spirit) for several products, such as whisky, gin, rum, brandy, and for different mixed-recipes. Similarly, another important industry is brewing, which produces a large volume of beer annually. The main ingredient used as the raw material for the production of potable alcohol in both industries, is barley grains. In a conventional production process, barley grains are mashed and fermented to produce an alcohol/water solution that is then distilled to concentrate the alcohol, if it is used for making spirit. A summarised description of the process is that

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http://dx.doi.org/10.1016/j.wasman.2017.02.018
0956-053X/

Fig. 1. BSG sample from Bushmills Distillery, Northern Ireland, UK (http://www.bushmills.com).

first the barley grains are ground to a coarse flour or 'grist' that is then mixed with hot water in a large mixing vessel, or a mash tun, to produce a sweet liquid called 'wort'. The sugars in the wort are essential in obtaining alcohol in the next stage. Yeast is added to this sweet malty liquid wort, which starts alcoholic fermentation for the conversion of the wort's sugars into alcohol (http://www.bushmills.com). The use of barley in this process generates a substantial amount of residual by-product, generally referred as spent barley grains (BSG).

It is a significant by-product in the overall brewing process, accounting for approximately 85% of total by-products, contributing to on average 30–60% of the biochemical oxygen demand and suspended solids (Fillaudeau et al., 2006). BSG is generated on average 31% of the original malt weight, therefore, it is necessary to overview all options available for the recycling of this residue for the economical processing and bioconversion into added-value products.

Fig. 1 shows BSG collected from a local licensed distillery – The Old Bushmills Distillery, Northern Ireland (http://www.ballycastle.info/places/distillery/distillery.htm). This solid residual material BSG is being used as a substrate in one of our current biotechnology research projects.

2. Recycling of BSG

The significant quantity of this by-product generated in distilleries and breweries can be utilised as a valuable bioresource, which is produced annually in many countries. The traditional method used at many places is composting, which is a simple low-cost treatment for the utilisation of this residue.

Composting is also an environmentally acceptable technology to convert this material into useful agricultural product, thereby eliminating profitless conventional landfilling. For composting purpose the nitrogen deficit in barley wastes can be supplemented with a co-composting material such as solid or liquid poultry manure (Guerra-Rodríguez et al., 2006). EU legislation, through the Council Directive 1999/31/EC, states that the amount of biodegradable organic waste that is disposed in landfills should be decreased by 65% by July 2016, relatively to the total amount of organic fraction of municipal solid waste (OFMSW) produced in 1995 (Neves et al., 2006).

Therefore, there is a great political and social pressure to reduce the pollution arising from industrial activities. Almost all industries in developed and developing countries are working to act on this issue by modifying their production strategies so that the by-products and residues of production system can be recycled, emphasizing to the point of focus on **"Reuse and not to waste"**. Consequently, most large companies no longer consider residues as a **"waste"**, but as a **"raw material"** for their use in other processes (Mussatto et al., 2006; Nigam and Pandey, 2009a,b; Ward and Nigam, 2009).

The barley wastes can be used as a carbon source in fermentation for microbial-biomass cultivation, production of microbial-enzymes, sugars, proteins, organic acids, antioxidants and food additives (Nigam and Luke, 2016), or simply as an adsorbent for removing organic materials from effluents and immobilization of various substances (Aliyu and Bala, 2010). There have been several efforts made to find an alternative use for barley waste. This overview describes the possibilities of utilisation of the barley waste for few value added products, the current knowledge for its bioprocessing is mainly focused for its bioconversion into animal feed, production of value-added compounds, such as xylitol, enzymes and lactic acid (Fig. 2).

3. Added-value products

Currently, there is an increased focus on minimizing the wastes generated by industries. In this overview, we have focused on two large-revenue industries – Distillery and Brewery, both generate a large amount of residual-mass; in form of brewers' spent grain (BSG). The production of BSG in Europe itself is approximately over 3.4 million tons (Stojceska et al., 2008). BSG is the most abundant brewing by-product, comprising of 85% of the all by-products generated, 31% of original malt weight and 20 kg per 100 l of beer produced. Therefore, a significant amount of this by – product is available for the potential production of bio-industrial product, such as ethanol through biotechnology, but in many regions its conventional reuse is still as animal feed, or landfill refuge (Buffington, 2014).

With respect to animal feed, BSG has been found to be an excellent feed source for ruminants. Beyond its reuse as an animal food product, some of its components could be useful as precursors for

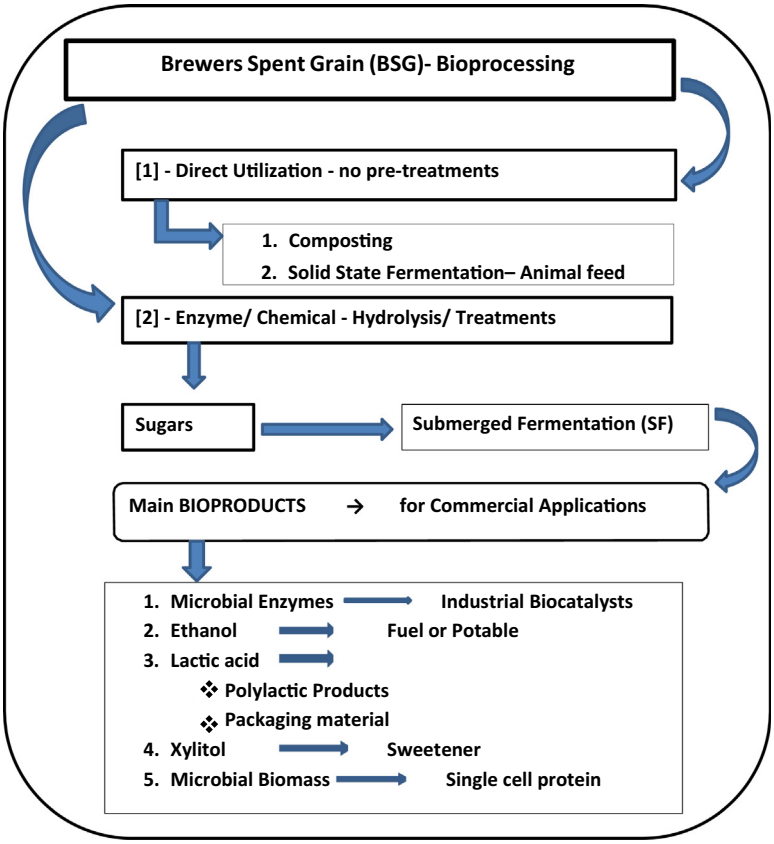

Fig. 2. Bioprocessing options for BSG generated in Distillery and Brewery.

food grade chemicals or as carbon source for microbial fermentations (Gupta et al., 2010).

This overview has particularly described two main approaches for waste barley to be used as a useful resource-material:

1. Dietary and nutritional application.
2. Microbial products for commercial/industrial uses.

4. Dietary and nutritional application

The approximate composition of barley waste comprises of protein (15–26%), lipids (3.9–10%) and 70% fibres, consisting of cellulose (15–25%), hemicellulose (28–35%) and some lignin (Aliyu and Bala, 2010). However, high moisture content of barley residues (~80%) together with polysaccharides makes it particularly susceptible to microbial growth, and can cause its spoilage in a short period of storage time of 7–10 days (Stojceska et al., 2008); therefore, making it necessary to establish a conservation process before or during the storage of wet BSG. The main nutritional application of barley waste in many countries has been selected to its use as animal feed (Mussatto, 2009). Distillery by – products (BSG and yeast cells recovered after the alcoholic fermentation) are best suited for their use in ruminant diets. As a good combination mixture of both, this feed provides protein with digestible fibres, present in barley residue. This mixed feed is highly palatable with very few limiting factors to feeding in ruminants. In contrast, it has limited use in pig and poultry rations due to low energy density and high level of fibre content. It is noted that the use of barley wastes for animal feed decreases the cost of feeding (Aliyu and Bala, 2010).

Belibasakis and Tsirgogianni (1996) studied the effect of BSG supplemented cattle feed on milk yield and its composition, and the blood components of dairy cattle fed with BSG feed. The study showed the treatment group was benefitted with an increased milk yield, milk fat and total milk-solids content, though the blood analysis for glucose, cholesterol, and sodium showed no effect. Feed trade sources reported that availability of distillery by-products in feeds was at a high level in year 2012, and its usage in animal feed has increased by 51% since 2007. Industrially produced lysine and threonine are added in the animal feed compositions using barley grain to obtain a balanced nutritional diet. However, the essential amino acids is added at additional cost. Other non-essential amino acids such as glutamine and proline are present in excess in the major storage proteins and create a different problem. These amino acids, when digested by the animal, release non-utilizable nitrogen. This nitrogen is excreted in the urine, which could create a significant environmental load, especially on and around pig farms (Arvanitoyannis and Tserkezou, 2007).

In addition to its use as an animal feed, in other nutrition application BSG have been incorporated into foodstuffs for human consumption, especially where there is a requirement to enhance or upgrade the fibre contents of certain food items; such as breads and snacks (Aliyu and Bala, 2010). The ingestion of barley grains or its derived products in form of high-fibre cookies containing BSG have been tested to provide health benefits (Prentice et al., 1978). The uptake of dietary fibre has been generally related to help in some non-infectious diseases, such as ulcerative colitis; Kanauchi et al., (2001) have developed functional germinated barley food stuff from brewer's spent grains. Barley residue was evaluated for its potential as a functional baking ingredient showing that an addition of 25% and 35% BSG significantly increased the protein content of the snacks, and the addition of 15% doubled the content of dietary fibre (Ktenioudaki et al., 2012). Though, an examination of samples of baked products for their aromatic com-

position revealed that the addition of BSG altered their odour profile. Whereas the sensory-test results of these food products indicated that BSG containing food materials with 10% amount of BSG were highly acceptable (Ktenioudaki et al., 2013).

In some food products, the maize flour from the chickpeas was replaced with BSG at levels of 10, 20, 25 and 30%. The effect of barley supplementation was studied on texture, colour, moisture, fat, fibre, starch, protein, phenolic compounds and antioxidant capacity of finished product (Ainsworth et al., 2007). With increasing levels of BSG addition, the percent of protein, fat and fibre content increased, while the overall starch content decreased. It was suggested that foods fortified with BSG be considered as functional foods. This may provide a number of health benefits; due to the fact that the dietary fibres have been reported to aid in the prevention of cancer, gastrointestinal disorders, diabetes and coronary heart disease (Stojceska et al., 2008).

Furthermore, BSG were evaluated as a promising source of lipids, this finding suggested that BSG could be considered for its utilisation in food industry (del Río et al., 2013). The results of this study revealed that the predominant lipids in BSG were triglycerides (67% of total extract), followed by a series of free fatty acids (18%), and also lower amounts of monoglycerides (1.6%) and diglycerides (7.7%). In studies by Niemi et al. (2012, 2013), barley lipids were analysed by pyrolysis-GC/MS after enzyme-aided solubilisation, showing that the most abundant lipids were linoleic (18:2), palmitic (16:0), and oleic acids (18:1), and small amounts of other fatty acids, such as stearic (18:0) and linolenic (18:3) acids, were present. These results suggest the potential for the supplementation of BSG in food preparations as the source of lipids.

5. Microbial products

Although the quality of BSG is regulated by its composition of barley grain husk, pericarp and fragments of endosperm, it defers slightly based upon the barley type, harvest time and mashing conditions (Forssell et al., 2008), but still the total carbohydrate content comprise of half of the dry mass of BSG. Therefore, the carbohydrate content makes BSG a potential substrate for various applications; the sugars that are released after chemical or enzymatic processing, can be microbiologically converted into various bioproducts, such as organic acids, ethanol, glycerol, food additives and butanol, etc. (Fig. 2). The use of BSG as a substrate in growth medium for a variety of suitable microorganisms provides a cheaper carbon source than defined media for economical production of a desired product. The growth medium is constituted to support the growth of a respective microorganism to generate a valuable product. Following sections describe some of microbial products, which can be synthesized using BSG as a cheaper raw material.

5.1. Bioethanol production

Due to fact that cellulose is the most abundant renewable natural biological resource; the barley residues of distillery and brewery industry containing appreciable amount of cellulose are the potential sources of feedstock for the production of bioethanol. The production of fuel ethanol is predominantly from agricultural crops rich in cellulose and starch (Aggarwal et al., 2001a,b), conventionally, alcohol biofuels have been produced on industrial scales by fermentation of sugars derived from wheat, corn, sugar beets, sugar cane and molasses. Such commercially produced biofuels have a drawback of their dependence on food crops (Gnansounou, 2010; Nigam and Singh, 2011). Hence, there is a need to promote a faster deployment of sustainable second generation bioethanol that will not compete with human food production (Singh et al., 2011a–c). With the increasing demand for ethanol, there is not only search for cheaper, abundant and annually renewable substrates; but also for the development of an efficient and less expensive technology so that ethanol can be made available at a lower cost from barley wastes (Shindo and Tachibana, 2006; Nigam and Singh, 2011; Singh and Nigam, 2014). Therefore, an alternative method has been proposed through the residual biomass utilisation in barley spent grain by economical bioprocessing. Second Generation Ethanol Production from Brewers' Spent Grain has been discussed by Liguori et al. (2015).

Data is available on composition of BSG consisting of grain husks and other residual compounds, the main ingredients are hemicelluloses, cellulose and lignin (Kanauchi et al., 2001; Mussatto et al., 2006). Cellulose, a D-glucose polymer, with β-1,4 glycosidic bonds existing in crystalline and amorphous forms, constitutes the main carbohydrate (carbon) source in these wastes, and therefore, it is ideal for ethanol production. The conditions required for the hydrolysis of lignocellulosics, and the factors affecting bioprocessing using microorganisms and cellulase enzymes have been researched comprehensively. Pre-treatments such as alkali, acid, steam explosion, and microwave pretreatment etc. have less or more impact on cellulose processing of several substrates (Kumar et al., 2009; Medina et al., 2016; Mosier et al., 2005; Zhu et al., 2006).

The bioprocess for the conversion of BSG to ethanol requires chemical or enzymatic hydrolysis to produce major fermentable sugars, followed by microbial fermentation. Since, the large amounts of enzymes are required for enzymatic saccharification of hemicellulose and cellulose to fermentable sugars, this process impacts severely on the cost effectiveness of this technology (Xiros et al., 2008), there are several studies about microbial fermentation that do not require a prior hydrolysis. An efficient and economical bioethanol production is possible in a process of simultaneous saccharification and fermentation (Singh et al., 1995; Verma et al., 2000).

The ethanol production by the mesophilic fungus *F. oxysporum* by coupling solid state and submerged bioreactor fermentation was investigated by Xiros and Christakopoulos (2009), these studies concluded that it was possible to control simultaneous production of cellulolytic and hemicellulolytic enzymes by *F. oxysporum*. This multi-enzymatic system was capable of hydrolyzing lignocellulosic substrate in a growth medium consisting of BSG under submerged conditions. In a different study, a consolidated enzymatic system of *Fusarium* and *Saccharomyces* was used to enhance the production of ethanol from BSG (Agarwal and Dinker, 2013). The combination of *Fusarium* culture with the *Saccharomyces* cultures proved to be very efficient in the simultaneous saccharification and conversion of produced sugars to bioethanol. Ethanol yield of up to 57% was obtained in a bioreactor fermentation system employing mixed culture. BSG have also been used as a cheaper supporting matrices for the immobilisation of yeast cells instead of synthetic polymers, and such prepared biocatalysts were successfully used as starter cultures for wine making and beer production (Tsaousi et al., 2010, 2011).

5.2. Lactic acid production

Lactic acid (2-hydroxypropionic acid) is a hydroxycarboxylic acid with many applications in food, pharmaceutical, textile, leather, chemical, cosmetic, and polymer industries (Nigam, 2009). The opportunities for industrial production of lactic acid lies in four categories: 1. Biodegradable polymers; 2. Oxygenated chemicals; 3. Green chemicals or solvents; 4. Plant-growth regulators. The importance of lactic acid has been increasing in the last few years as it can be used as a precursor of poly-lactic acid

(PLA) production), which leads to bio-plastic applications and has been produced using hydrolysate of corncob (Bai et al., 2008). In particular, lactic acid has found applications relative to food, pharmaceuticals and chemicals (Ali et al., 2007).

Brewer's spent grain has found a prominent application as a raw material for lactic acid production in a bioprocess employing *Lactobacillus delbrueckii* (Nigam, 2009; Mussatto et al., 2008). The biosynthesis of lactic acid from any lignocellulosic material can be performed using sequential steps, such as: chemical processing – in order to make the cellulose more accessible to the enzymes; enzymatic hydrolysis – to obtain saccharified-solution containing glucose as the main sugar, and in final step, the fermentation of hydrolysate by suitable and effective microorganisms, especially *Lactobacillus* species.

However, the lactic acid production by microorganisms is influenced by several experimental conditions, including pH, agitation speed, carbon source, temperature, medium composition, inoculum size and age, aeration rate, initial sugar concentration and fermentation mode (continuous, or batch/fed-batch fermentations) (Hofvendahl and Hahn-Hägerdal, 2000). Raw material for industrial lactic acid production ideally must have desirable properties, such as low cost, low levels of contaminants, a fast fermentation cycle, high yields of lactic acid, a relatively low levels of by-products formation and year-round availability of the material at low cost (Nigam, 2009). Lactic acid production is a good option using BSG as substrate in solid state fermentation employing fungal cultures. Strains of *Rhizopus* sp. have been most commonly used among other fungal cultures by Koutinas et al. (2007a, 2007b). The time required to complete solid state fermentation for lactic acid production is usually 120–200 h. Effects of cultivation parameters on morphology of *Rhizopus arrhizus* and lactic acid production in a bubble column reactor has been studied by Zhang et al. (2007). For submerged lactic acid fermentations bacterial cultures are more efficient. *Lactobacillus casei* has been reported to produce higher concentration of lactic acid in comparison to *Lactobacillus helveticus* and *Streptococcus thermophiles.* A comprehensive information is available on lactic acid production utilising residues in economical bioprocessing through microbial conversions (Nigam, 2009).

5.3. Xylitol production

Xylitol is an important alternative to sucrose as a sweetener with many applications in the food industry, and hence, microbiological production of xylitol has been studied using efficient microorganisms (Nigam et al., 2004; Nigam and Singh, 1995). Xylitol can be produced by fermentation from xylose using acid hydrolysates of waste BSG (Aliyu and Bala, 2010). During the fermentation it is necessary to use a microorganism that will have capability to convert xylose into xylitol.

Carvalheiro et al. (2005, 2007) and Duarte et al. (2004) showed that using spent grains, the strain of *Debaryomyces hansenii* could produce xylitol and arabitol, as the major fermentation products together with some ethanol and glycerol. After the optimisation of the acid hydrolysis conditions of barley wastes, a xylitol yield and productivity of 0.70 g/g and 0.45 g/l h, respectively, could be attained during fermentation of hydrolysate by yeast. Mussatto and Roberto (2005) used *Candida guilliermondii* to produce xylitol from the BSG hydrolysate and found the overall results to be economically feasible. The bioprocesses using microorganisms are more effective in producing higher xylitol yields. The use of hemicellulose for xylitol fermentation means that residues such as barley wastes from distilleries and breweries, are good substrate for xylitol production. Although xylitol production by biological processes has been found effective but for adequate industrial scale production, the reater understanding of factors affecting the xylitol synthesis process is necessary (Nigam et al., 2004).

5.4. Microbial enzyme production

It is well known that enzyme production on industrial scale using defined media incorporates a high cost of production, thus the utilisation of waste barley grains as the cheaper raw material could be the key to reduce the overall costs, and making the enzyme production more profitable (Nigam and Pandey, 2009a, b). The carbohydrate composition of barley residues makes this waste a suitable substrate for the production of various enzymes. Brewery spent grains have been used as substrate for the production of cellulases by a strain of cellulolytic fungus *Trichoderma reesei* (Sim and Oh, 1989). BSG has been found an efficient substrate for xylanase production by a *Streptomyces* isolated from Brazilian cerrado soil (Nascimento et al., 2002), and for the production of xylanase and feruloyl esterase by *Streptomyces avermitilis* (Bartolomè et al., 2003). It has been reported that BSG was as an efficient substrate utilised by fungal species, such as *Pleurotus ostreatus* (Gregori et al., 2008), and *Penicillium janczewskii* (Terrasan et al., 2010) for the production of several enzymes. BSG has been used as substrate for the production of enzyme xylanase cultivating a fungus *Penicillium glabrum* by Knob et al. (2013). Higher overall yields, higher specific activity of purified xylanase, low cost of feedstock and conventional purification method proved BSG as a potentially useful material for this biotechnological process.

6. Other uses of BSG

BSG can be used for protein hydrolysate production, as the barley waste may consist of 10–24% protein content on a dry weight basis (Robertson et al., 2010). The lack of protein solubility is one of the limitations for its more extensive use in food processing. Barley wastes can be treated mainly in enzymatic or alkaline hydrolysis, in order to release proteins. A treatment of milled barley waste grains was carried out with a preparation of carbohydrase enzyme mixture produced by *Humicola insolens*, which significantly improved the solubilisation of protein from residual biomass. Furthermore, 76% of the protein was solubilised after a treatment with an alkaline protease (Niemi et al., 2013). A gel permeation HPLC analysis of the protein-rich isolate after the alkaline extraction (110 mM NaOH) showed that the most prominent amino acids were glutamine/glutamate and proline (Connolly et al., 2013). Vieira et al. (2014) designed a sequential extraction of proteins and arabino-xylans from BSG; with increasing strength of alkali solution used, extraction resulted in a yield of 82–85% in total proteins and 66–73% of total arabino-xylans. Such hydrolysates from BSG were used as a protein supplement in a simple growth medium for the growth of *Streptomyces* (Szponar et al., 2003), *Bifidobacterium adolescentis* 94BIM, and *Lactobacillus* sp. (Novik et al., 2007).

7. Conclusions

The necessity for this overview was to study the options available for the recycling of BSG for its economical bioconversion into added-value products. This major by-product of distilleries and brewing industry has a considerable potential for its utilisation as described in this overview. Depending on the expertise and facilities available at the site of its recycling, BSG can be utilised through the biotechnological processes; as a low-cost material for various purposes. A strategy for its utilisation and conversion

should be decided according to the scale of availability of this residual-biomass in the proximity of the processing facility.

Acknowledgment

BSG was kindly provided by The Old Bushmills Distillery, Northern Ireland as gift for one of our current biotechnology research projects.

Writing of this overview did not receive any specific grant from funding agencies in the public, commercial or not-for-profit sectors.

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